CH-110 Advanced General Chemistry I

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Housekeeping notes

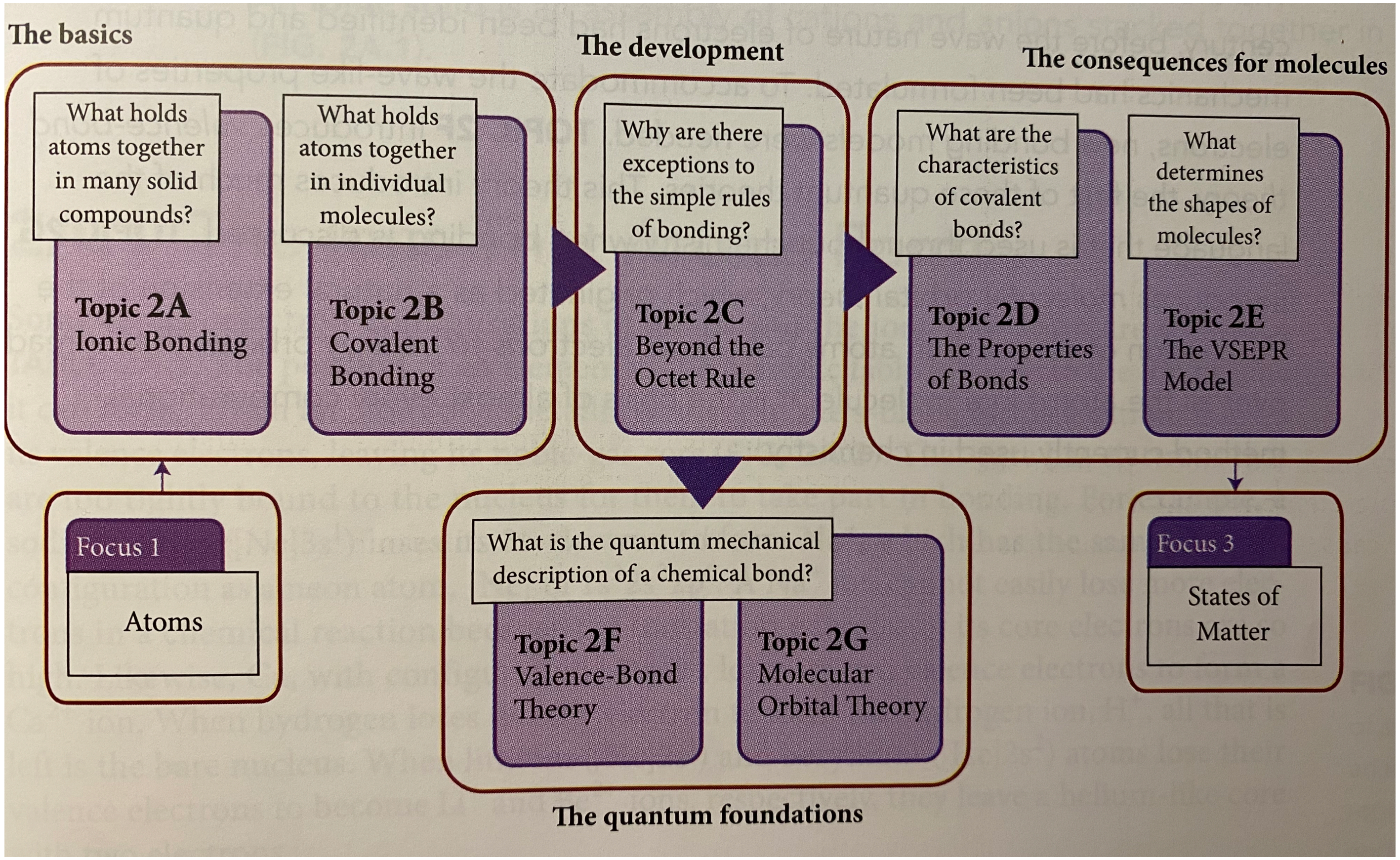
Q&A session:

- Class delegate: please contact me when you have your exam schedule to fix a date for the Q&A session, likely in mid-January.
- We will open a channel in the Ed discussion forum to post questions that need to be discussed during the Q&A session. We will **not** discuss anything unless you pose a **specific question**.
- Last exercise session is today.
- Urgent questions: you can continue to ask questions in the Ed discussion forum.

Student question

- **Question**: why do we draw spins up most of the time, but in VB theory, we sometimes draw them spin down?
- The two spin states (+1/2 and -1/2) are degenerate and energetically equivalent. You can theoretically choose if you draw them spin up or all down. What’s important is the relationship between spins: parallel vs. antiparallel. When electrons populate degenerate orbitals one by one, the spins are parallel, you can draw them ‘all up’ or ‘all down’, by convention usually they are drawn ‘all up’. For bonding, you need antiparallel spins. So if you show one atom with spins ‘all up’ and you combine them to form a bond with another atom, then the other atom needs to be drawn with spins down.

Overview Chapter 2 (Focus 2: Bonds Between Atoms)



The basics

What holds atoms together in many solid compounds?

Topic 2A Ionic Bonding

What holds atoms together in individual molecules?

Topic 2B Covalent Bonding

The development

Why are there exceptions to the simple rules of bonding?

Topic 2C Beyond the Octet Rule

The consequences for molecules

What are the characteristics of covalent bonds?

Topic 2D The Properties of Bonds

What determines the shapes of molecules?

Topic 2E The VSEPR Model

Focus 1

Atoms

What is the quantum mechanical description of a chemical bond?

Topic 2F Valence-Bond Theory

Topic 2G Molecular Orbital Theory

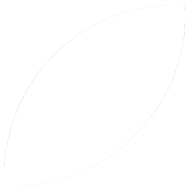
The quantum foundations

Focus 3

States of Matter

Molecular Orbital Theory

Topic 2E



Last Tuesday: Topic 2G.1 Molecular orbitals
Topic 2G.2 Electron configurations of diatomic molecules
Topic 2G.3 Bonding in heteronuclear diatomic molecules
~~Topic 2G.4 Orbitals in polyatomic molecules~~
Topic 2G.5 A comparison of bonding models

WHY DO YOU NEED TO KNOW THIS MATERIAL?

- MO theory is the most common quantum mechanical approach used to describe electronic structure of molecules.
- Essential for understanding the properties of individual molecules and modern materials.

WHAT DO YOU NEED TO KNOW ALREADY?

- Atomic orbitals (Topic 1D)
- Born interpretation of wavefunction (Topic 1C)
- Building-up principle (Topic 1E)
- Electronegativity (Topics 1F and 2D)

2G.1 Molecular orbitals

Valence bond theory deficiencies

We know that oxygen is paramagnetic:

https://www.youtube.com/watch?v=Lt4P6ctf06Q ←

Figure 2G.10 (new book)

- Attracted to magnetic fields
- O_2 must have unpaired electrons

→ This is not explained by VB theory. A new theory is needed.

2G.1 Molecular orbitals

Molecular orbital (MO) theory vs. valence bond (VB) theory

MO theory

- Addresses limitations of VB theory
- Provides a deeper understanding of electron-pair bonds
- Easier to calculate computationally than VB theory

In MO theory: electrons occupy MOs that are **delocalized** over entire molecule

In VB theory: electrons are **localized** between the two atoms

2G.1 Molecular orbitals

Molecular orbital (MO) theory vs. valence bond (VB) theory

Aspect	VB Theory	MO Theory
Wave Function Mixing	Combines atomic orbitals into hybrid orbitals	Combines atomic orbitals into molecular orbitals
Localization	Localized between specific atoms	Delocalized over the entire molecule
Bonding Description	Overlap of orbitals, hybridization sp^3, sp^2, sp	Bonding and anti-bonding orbitals, delocalized π bonds

2G.1 Molecular orbitals

Linear combinations of atomic orbitals

- **Making bonds = mixing wavefunctions of atoms**
- The technical term for adding together wavefunctions is «forming a linear combination».

$$\Psi = \Psi_{\mathrm{A}1s} + \Psi_{B1s}$$

- This equation represents a **linear combination of atomic orbitals (LCAO).**
- A molecular orbital formed from a linear combination of atomic orbitals on different atoms is called an **LCAO-MO**.

2G.1 Molecular orbitals

Linear combinations of atomic orbitals

- MOs are well-defined mathematical functions that can be evaluated at each point in space and pictured in three dimensions.
- The square of the wavefunction is the **probability density** for an electron that occupies it. Where Ψ^2 is large, the probability density is high.
- The precise form of the MO depends on the **internuclear separation**, which can be changed in the calculation to explore how its shape ad the corresponding energy vary with bond length.

2G.1 Molecular orbitals

Bonding orbitals

A combination of atomic orbitals that results in an overall lowering of energy, like that in Eq.1, is called a **bonding orbital**, **denoted $\boldsymbol{\sigma}$** (here σ_{1s}).

The combination of *N* atomic orbitals results in the formation of *N* molecular orbitals.

Hydrogen example: LCAO-MOs are built from two atomic orbitals, *two* molecular orbitals are formed.

Bonding orbital: $\boldsymbol{\Psi = \Psi_{A1s} + \Psi_{B1s}}$

Antibonding orbital: $\Psi = \Psi_{A1s} - \Psi_{B1s}$

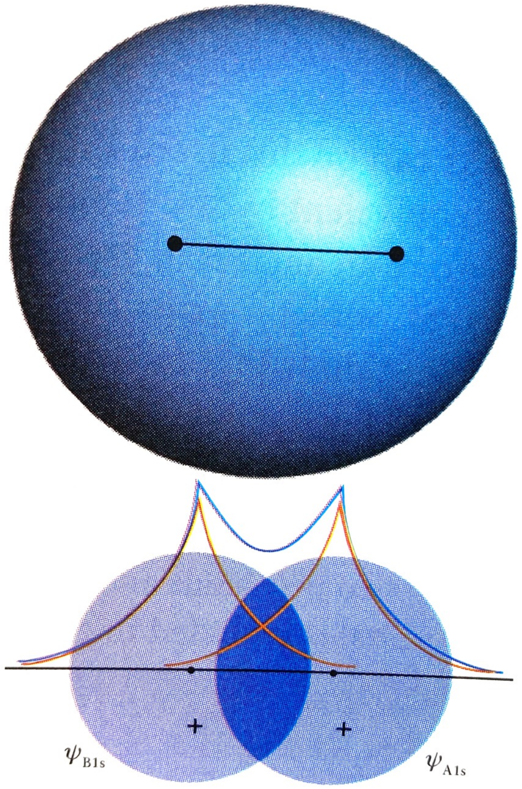


Figure 2G.1 (new book)

2G.1 Molecular orbitals

Antibonding orbitals

Bonding orbital: $\Psi = \Psi_{\mathrm{A1s}} + \Psi_{B1s}$

Antibonding orbital: $\boldsymbol{\Psi = \Psi_{\mathrm{A1s}} - \Psi_{B1s}}$

A negative sign indicates that the amplitude of Ψ_{B1s} **subtracts** from the amplitude of Ψ_{A1s} where they overlap. Subtraction leads to locations where the **AOs cancel completely**. A «nodal surface» is formed, a plane that lies halfway between two nuclei.

An electron that occupies that orbital is largely excluded from the internuclear space and has a **higher energy** when it occupies one of the atomic orbitals alone.

A combination of atomic orbitals that results in a higher energy than that of the original atomic orbitals is called an **antibonding orbital, denoted $\boldsymbol{\sigma}^*$** (here: σ_{1s}^*).

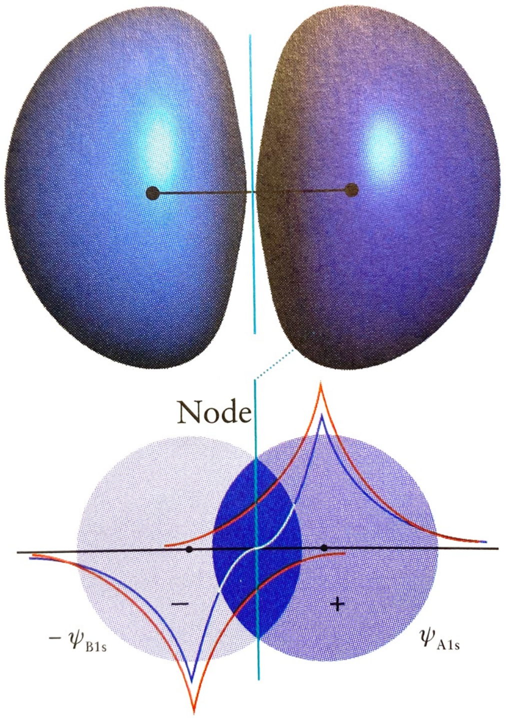
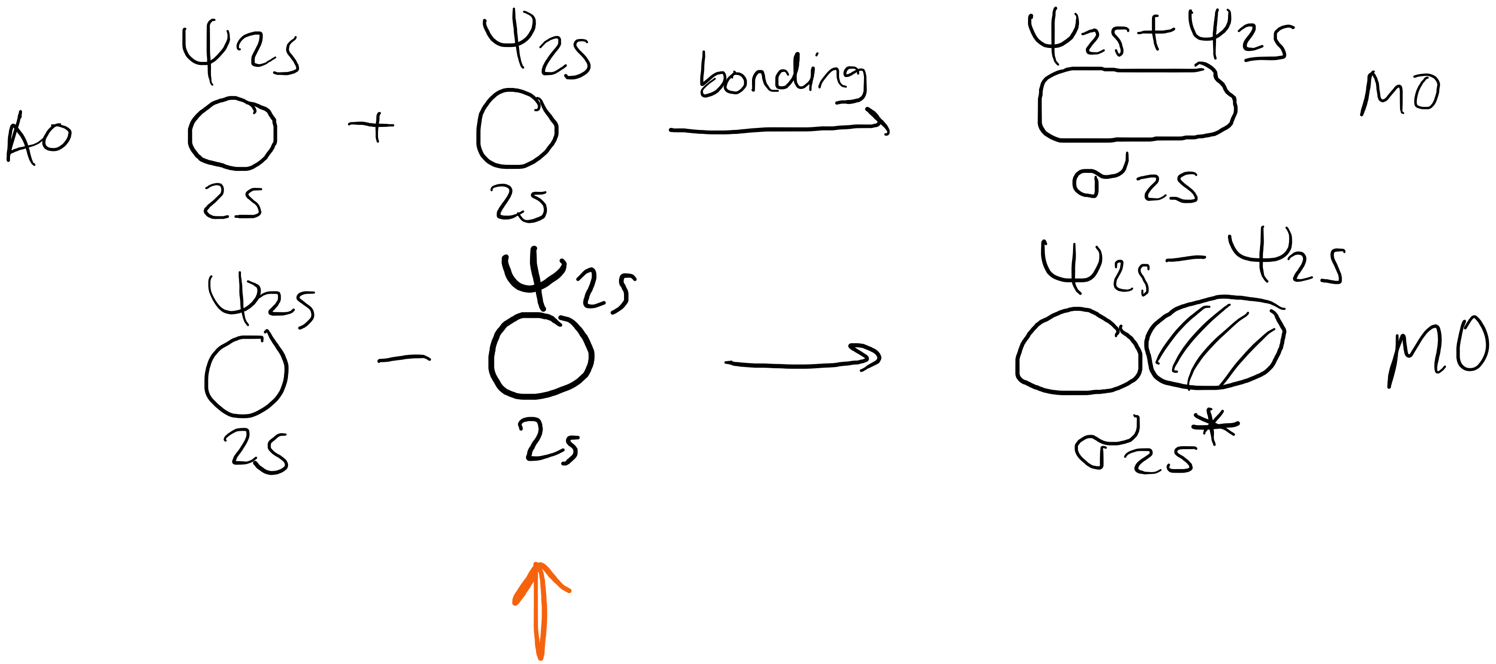


Figure 2G.2 (new book)

2G.1 Molecular orbitals

Molecular orbitals of Li_2

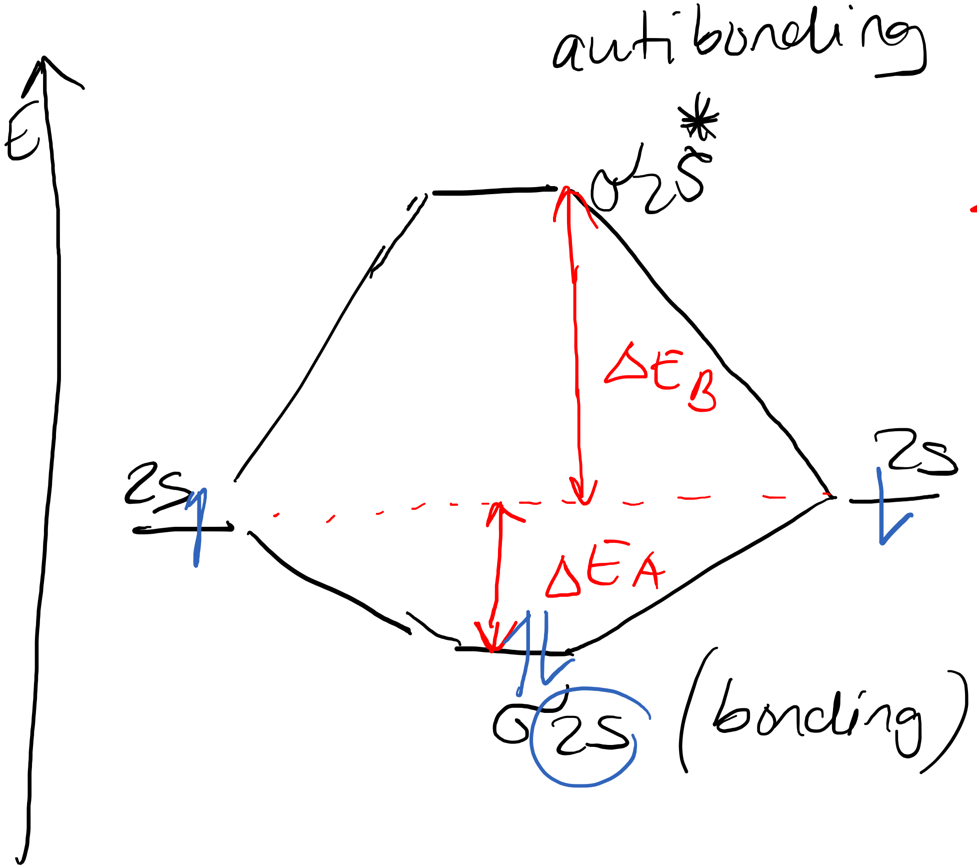
1 valence $e^{\ominus}$



mistake during lecture!

2G.1 Molecular orbitals

MO diagram of Li_2



$\Delta E_B > \Delta E_A$

Bond order:

$$b = \frac{1}{2}(N_e - N_e^*)$$

$$b(Li_2) = \frac{1}{2}(2 - 0) = \underline{\underline{1}}$$

2G.1 Molecular orbitals

MO diagrams

The relative energies of the original atomic orbitals and the bonding and antibonding molecular orbitals are shown in a molecular orbital energy-level diagram (**Fig 2G.3**)

- Diagram shows **relative energies** of AOs and MOs.

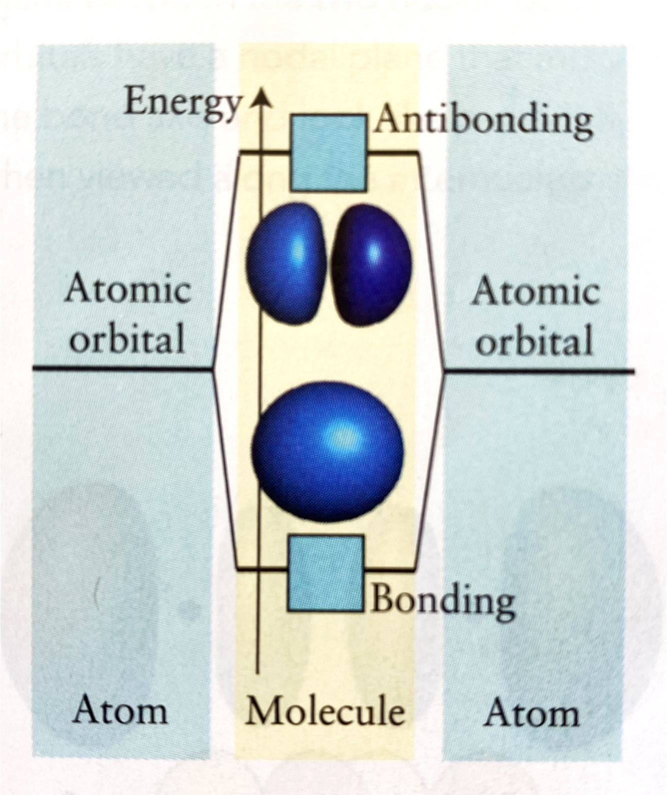


Figure 2G.3 (new book)

2G.1 Molecular orbitals

MO diagrams

- Increased energy of an **antibonding orbital is typically a little greater** than the lowering of the energy of the corresponding bonding orbital.
- Why? Although the bonding and antibonding orbitals have opposite effects on energy, the **repulsion between the nuclei** is the same in each case and pushes both orbital energies upward (Fig. 2G.4).

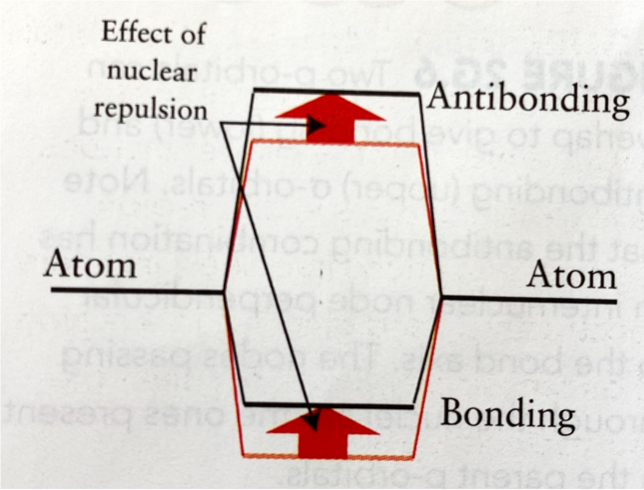


Figure 2G.4 (new book)

2G.1 Molecular orbitals

Drawing MO diagrams

MO theory adopts the approach used for **predicting the electron configurations of many-electron atoms** (Topic 1E) but applies it to **molecular orbitals** rather than atomic orbitals.

1. Form all the MOs that can be built from the available valence-shell atomic orbitals.

2. Populate them with the available electrons in the lowest-energy MO.

In MO theory:

- A σ-bond is a pair of electrons in a σ-orbital.
- The electron configuration of hydrogen is σ_{1s}^2.

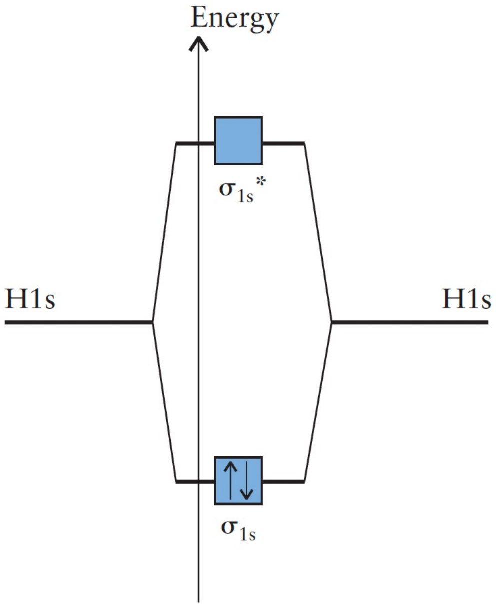


Figure 2G.5 (new book)

2G.1 Molecular orbitals

Summary

Molecular orbitals are built from linear combinations of atomic orbitals: when atomic orbitals interfere **constructively**, they give rise to **bonding orbitals**; when they interfere **destructively**, they give rise to **antibonding orbitals**. N atomic orbitals combine to give N molecular orbitals.

2G.2 Electron configurations of diatomic molecules

Procedure for determining the electronic configuration of diatomic molecules

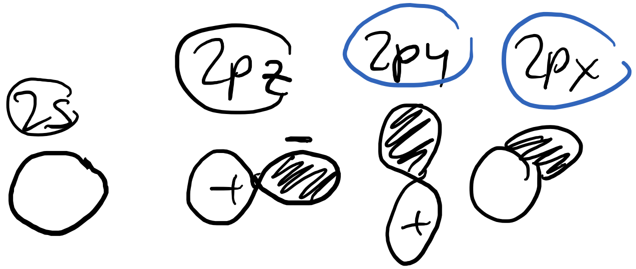
Molecular orbitals are built from all the available valence-shell atomic orbitals (occupied or not). Valence electrons are then accommodated in these molecular orbitals following these rules:

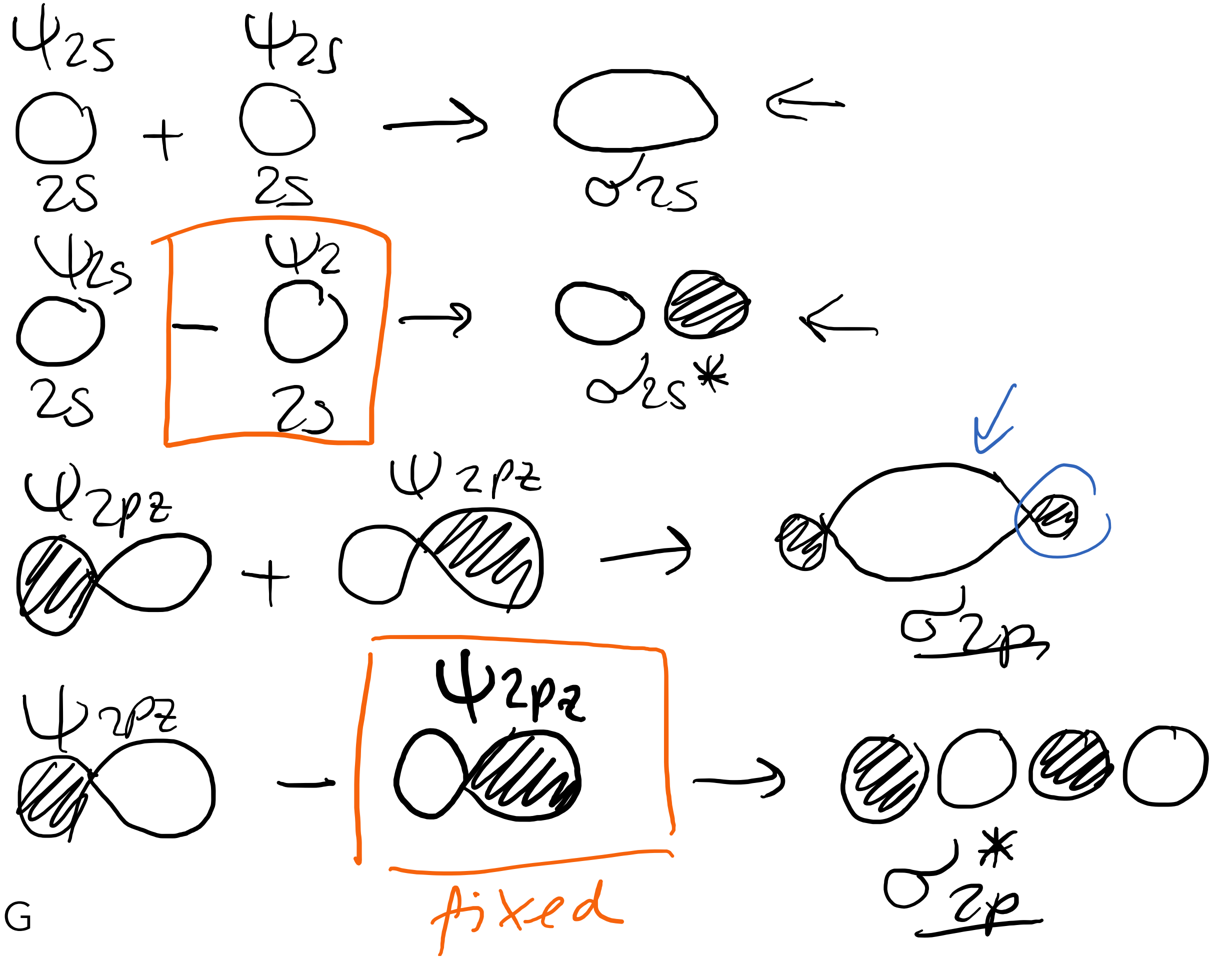
1. Electrons occupy the lowest-energy molecular orbital first, then occupy orbitals of increasingly higher energy.
2. According to the Pauli exclusion principle, each molecular orbital can accommodate up to two electrons. If two electrons are present in one orbital, their spins must be paired (↑↓).
3. If more than one molecular orbital of the same energy is available, the electrons enter them singly and adopt parallel spins (Hund's rule).

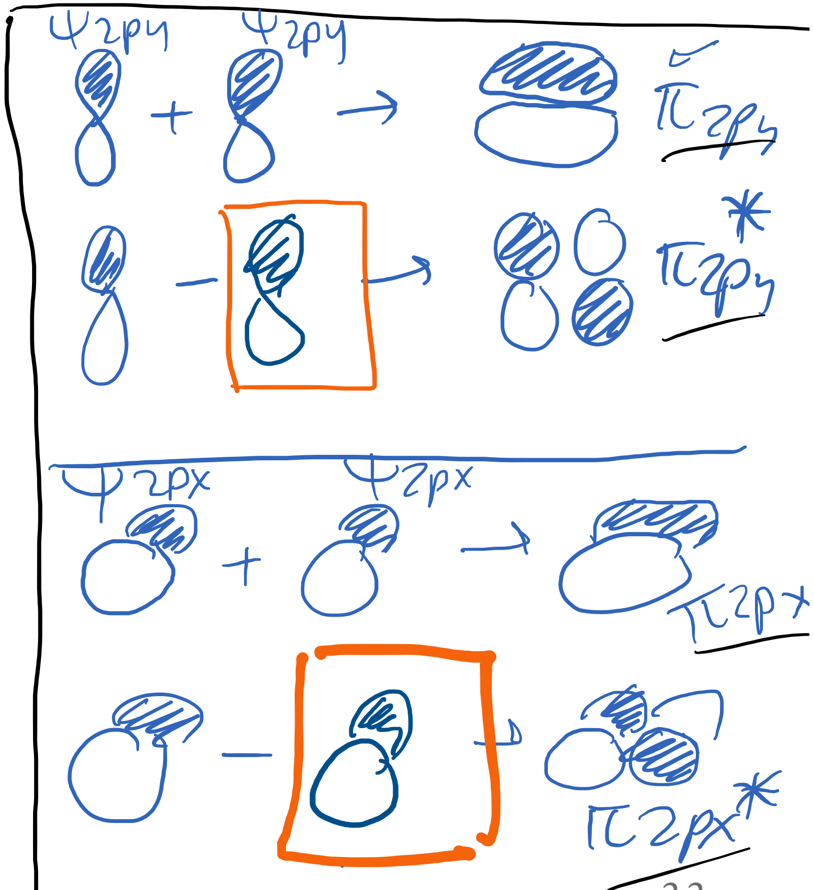
2G.1 Molecular orbitals

Molecular orbitals of O_2

$1 \times 2s, \quad 3 \times 2p$







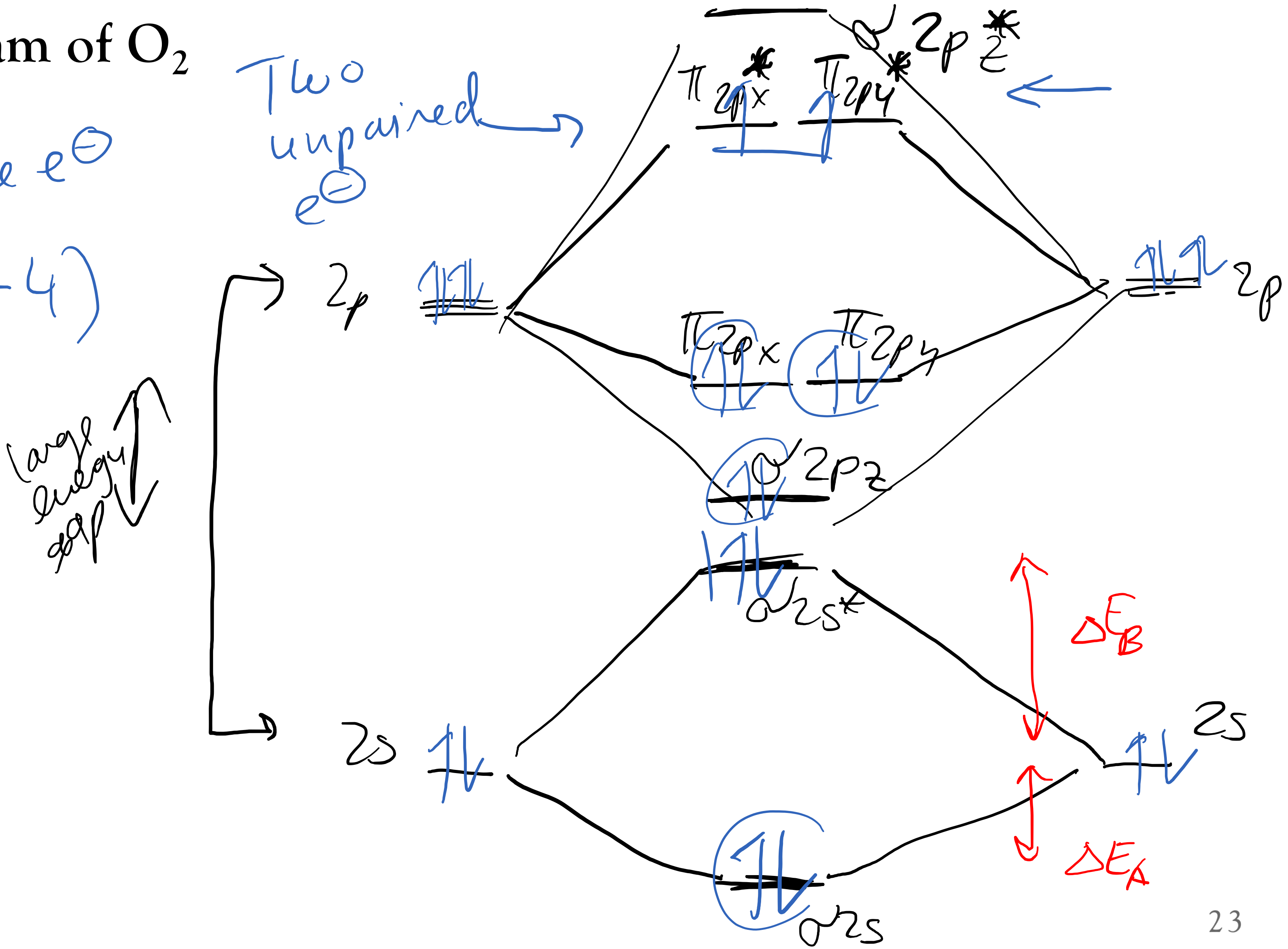
MO diagram of O_2

12 valence $e^{\ominus}$

$b = \frac{1}{2}(8-4)$

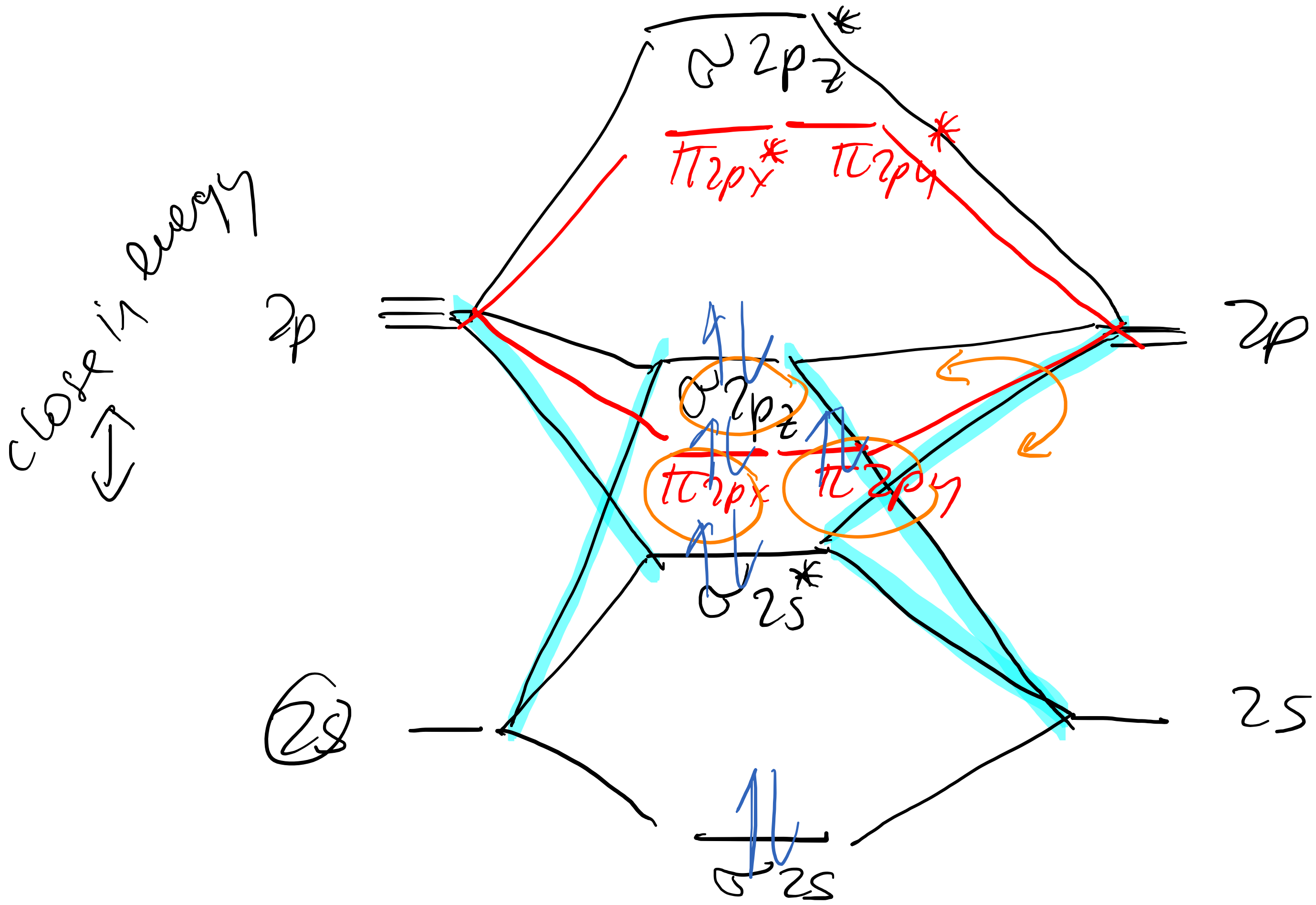
$= \underline{\underline{2}}$

O=O



MO diagram of N_2

2s & 2p are close in energy



$$b = \frac{1}{2}(8-2) = 3$$

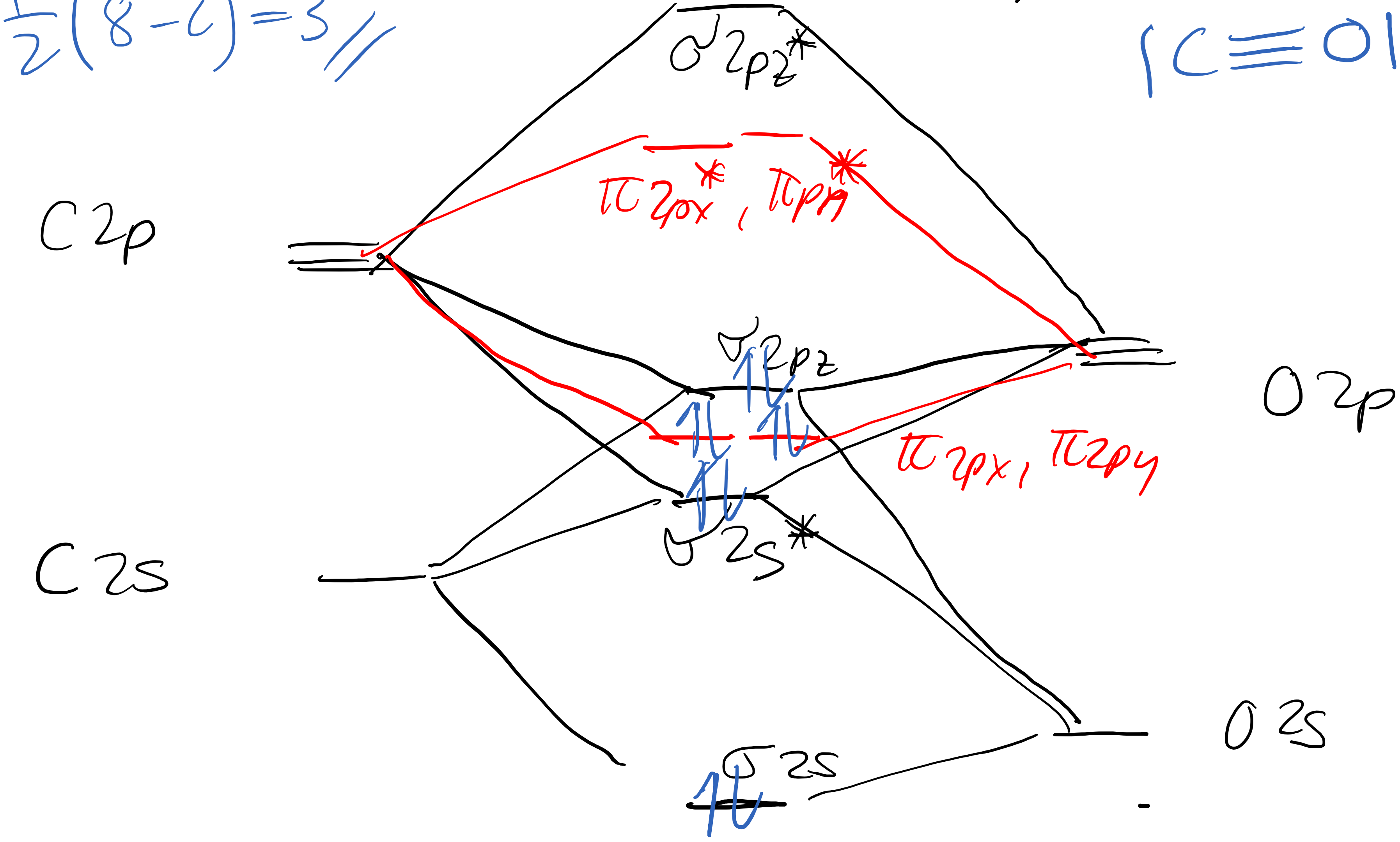
:N≡N:

MO diagram of CO

F O N Cl Br I S C H

$b=\frac{1}{2}(8-2)=3$ //

$|C\equiv O|$



2G.2 Electron configurations of diatomic molecules

Valence-shell MOs for Period 1 & 2 homonuclear diatomic molecules

- Period 2: 2s and 2p orbitals available (four atomic orbitals)
- For diatomic molecules: total of eight AOs available to form eight MOs
- The 2s-orbitals overlap to form two σ-orbitals : one bonding (σ_{2s}) and one antibonding (σ^*_{2s}) (resemble σ_{1s} and σ^*_{1s} in hydrogen molecule).

2G.2 Electron configurations of diatomic molecules

Valence-shell MOs for Period 1 & 2 homonuclear diatomic molecules

- Six 2p-orbitals (three on each atom)
- Overlap possible in two distinct ways:

1. End-to-end

Cylindrical symmetry, oriented along internuclear axis (one bonding, one antibonding)

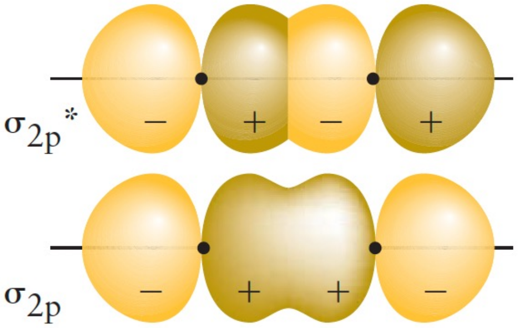


Figure 3.29 (old book)

2. Side-by-side:

- Oriented perpendicularly to internuclear axis

- Two bonding, two antibonding (only two shown here)

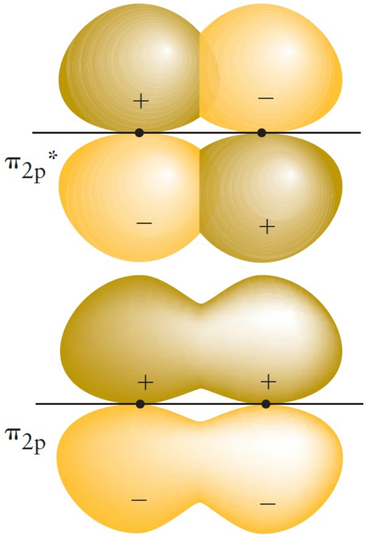


Figure 3.30 (old book)

2G.2 Electron configurations of diatomic molecules

Valence-shell MOs for Period 1 & 2 homonuclear diatomic molecules

- Six 2p-orbitals (three on each atom)
- Overlap possible in two distinct ways:

1. End-to-end

Cylindrical symmetry, oriented along internuclear axis (one bonding, one antibonding)

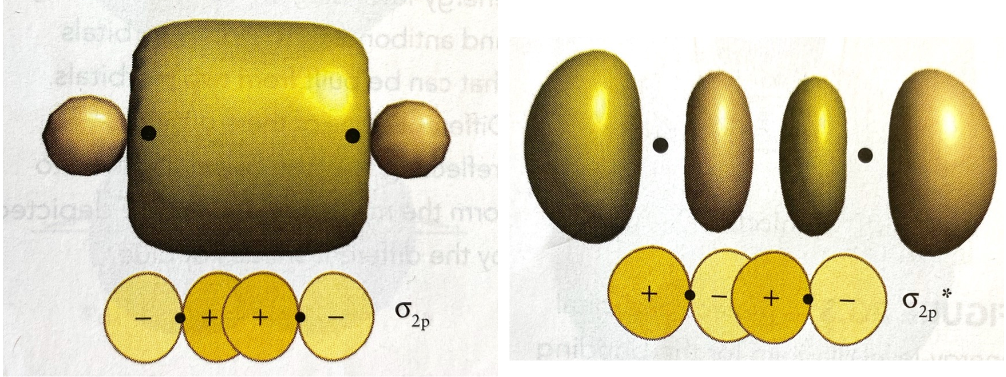


Figure 2G.7 (new book)

2. Side-by-side:

- Oriented perpendicularly to internuclear axis
- Two bonding, two antibonding (only two shown here)

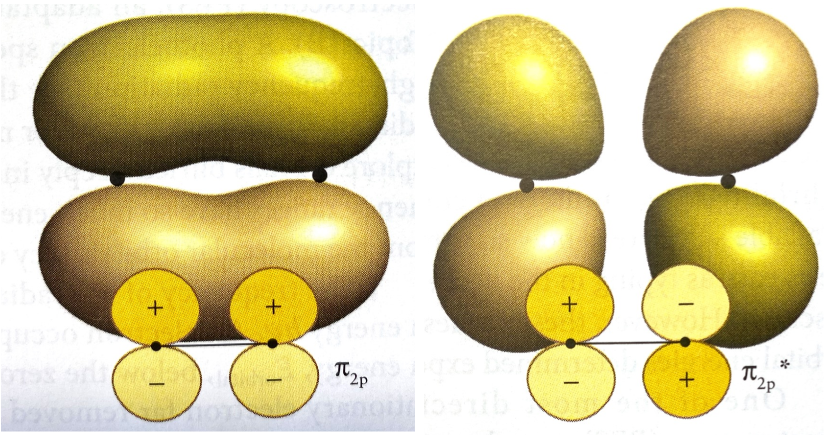


Figure 2G.8 (new book)

2G.2 Electron configurations of diatomic molecules

σ- and π-orbitals

- A **σ-orbital** is a molecular orbital that has **cylindrical symmetry** and **no nodal plane that contains the internuclear axis**.
- A **π-orbital** is a molecular orbital with a **nodal plane that contains the internuclear axis**.
- Both types of orbitals can be either bonding or antibonding:

  Bonding orbitals do not have internuclear nodes arising from destructive interference, antibonding orbitals do.

2G.2 Electron configurations of diatomic molecules

MO diagrams for homonuclear diatomic molecules

Li_2 to N_2

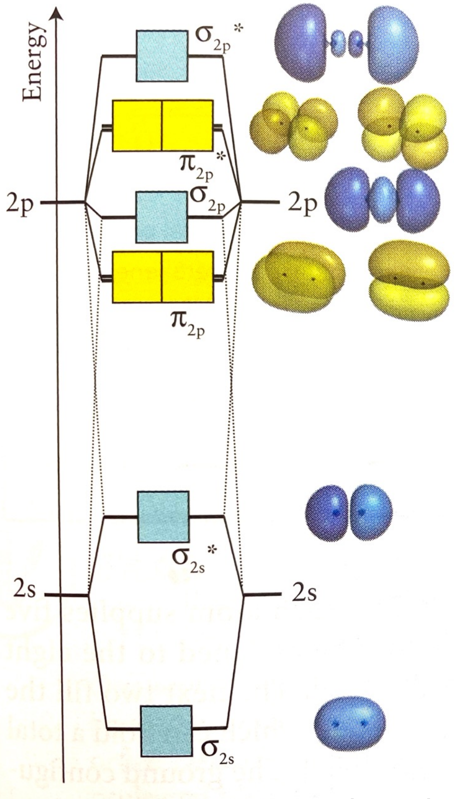


Figure 2G.8 (new book)

O_2 and F_2

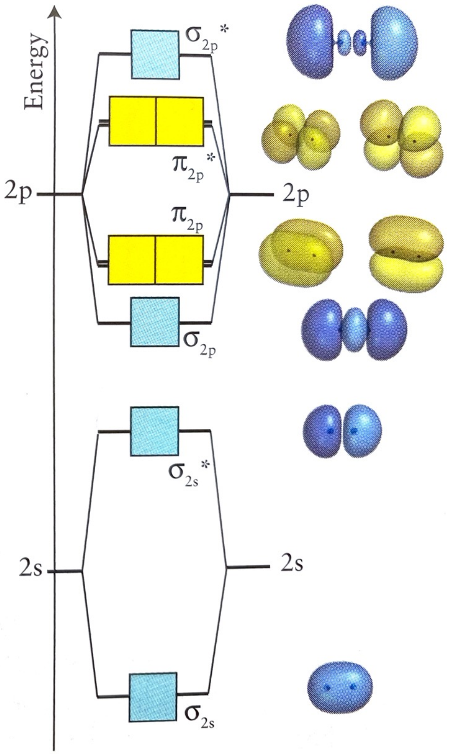


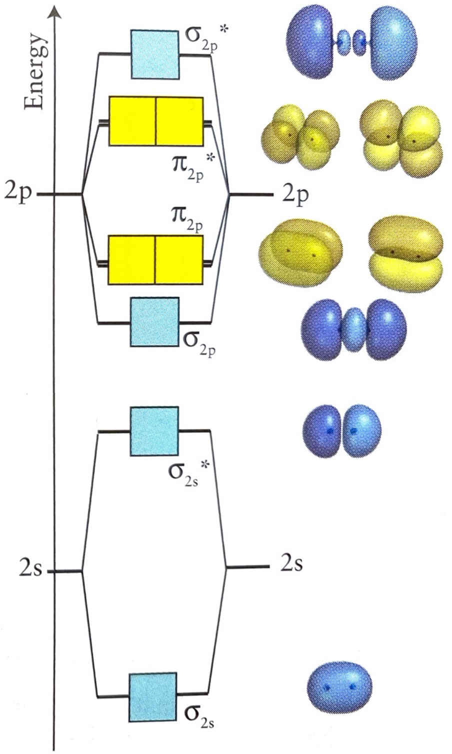
Figure 2G.9 (new book)

- Note: order of mixed molecular orbitals is different!

2G.2 Electron configurations of diatomic molecules

MO diagrams for homonuclear diatomic molecules

O_2 and F_2



- Note: order of mixed molecular orbitals is different!
- **O and F atoms** have many electrons that contribute to shielding. 2s and 2p orbitals are well separated.
- Order as shown:

$$\sigma_{2s} < \sigma_{2s}^* < \sigma_{2p} < \pi_{2p} < \pi_{2p}^* < \sigma_{2p}^*$$

Topic 2G

Figure 2G.9 (new book)

2G.2 Electron configurations of diatomic molecules

MO diagrams for homonuclear diatomic molecules

Li_2 to N_2

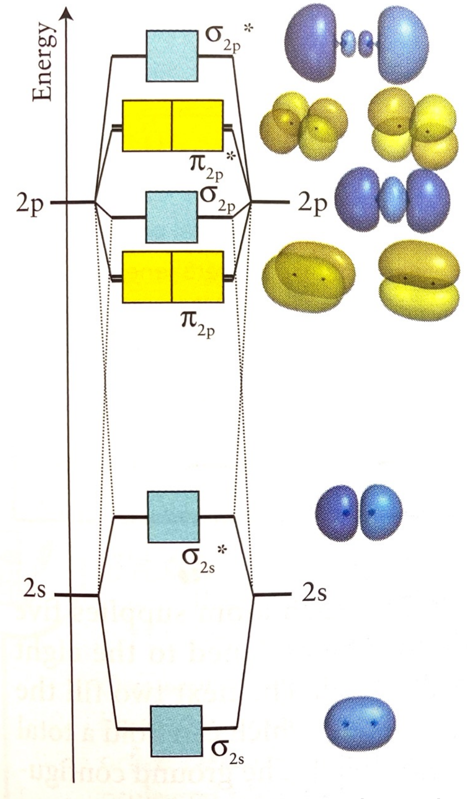


Figure 2G.8 (new book)

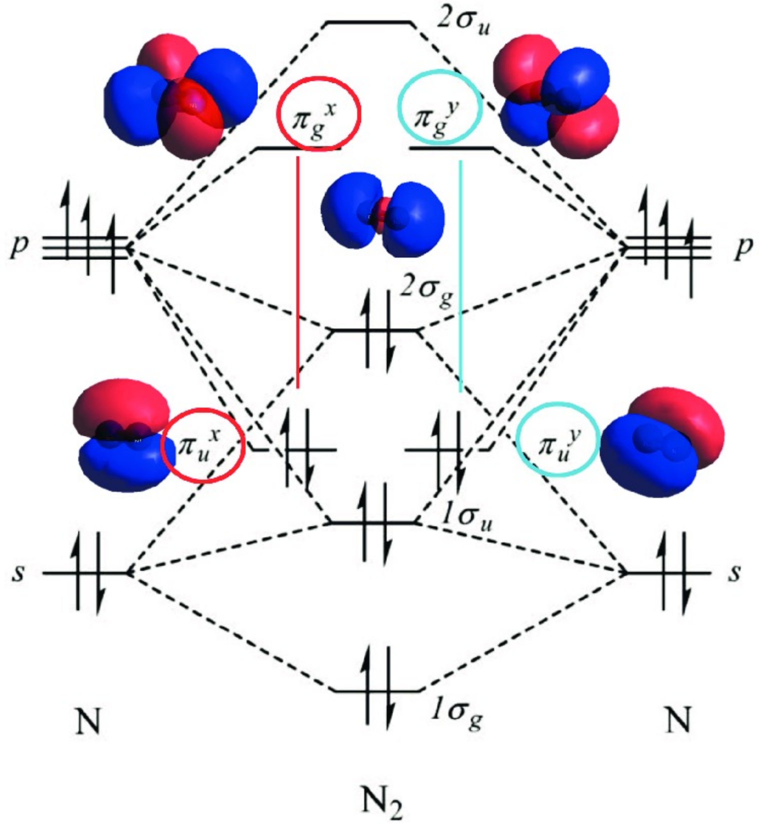
- Note: order of mixed molecular orbitals is different!
- **For Li to N**, these atoms have fewer electrons, less shielding: the 2s and 2p orbitals are similar in energy.
- The σ-orbitals for these molecules are formed by mixing both 2s/2p orbitals. **It is difficult to predict where the resulting σ-orbitals lie.**
- Experimentally, they turn out to lie as shown in Figure 2.8:

$$\sigma_{2s} < \sigma_{2s}^* < \pi_{2p} < \sigma_{2p} < \pi_{2p}^* < \sigma_{2p}^*$$

- You can think of it as 2s/2p orbitals all mixed together and split up together into four orbitals, whereas for O and F, the 2s mix separately to the 2p orbitals and split separately.

2G.2 Electron configurations of diatomic molecules

MO diagrams for homonuclear diatomic molecules



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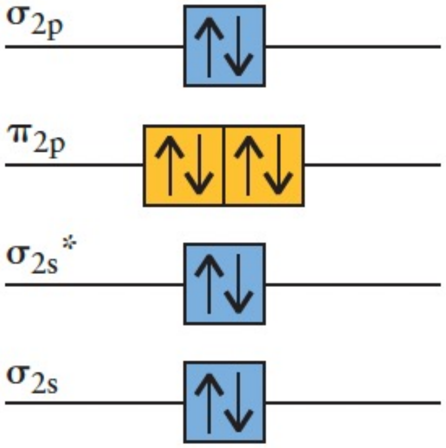
2G.2 Electron configurations of diatomic molecules

Ground-state electron configurations in MO theory

- Use building-up principle to accommodate all the valence electrons
- Each atom supplies five valence electrons
- Ten electrons assigned to orbitals shown in Figure 2G.8
- Electron configuration in ground state:

$$N_2: (\sigma_{2s})^2(\sigma_{2s}^*)^2\left(\pi_{2p}\right)^4\left(\sigma_{2p}\right)^2$$



45 Nitrogen, N_2

2G.2 Electron configurations of diatomic molecules

Bond order in MO theory

- In MO theory, the bond order, *b*, is defined as the net number of bonds, allowing for the cancellation of bonds by antibonds:

$$b = \frac{1}{2} \times (N_e - N_e^*)$$

Number of electrons in bonding orbitals: N_e

Number of electrons in antibonding orbitals: N_e^*

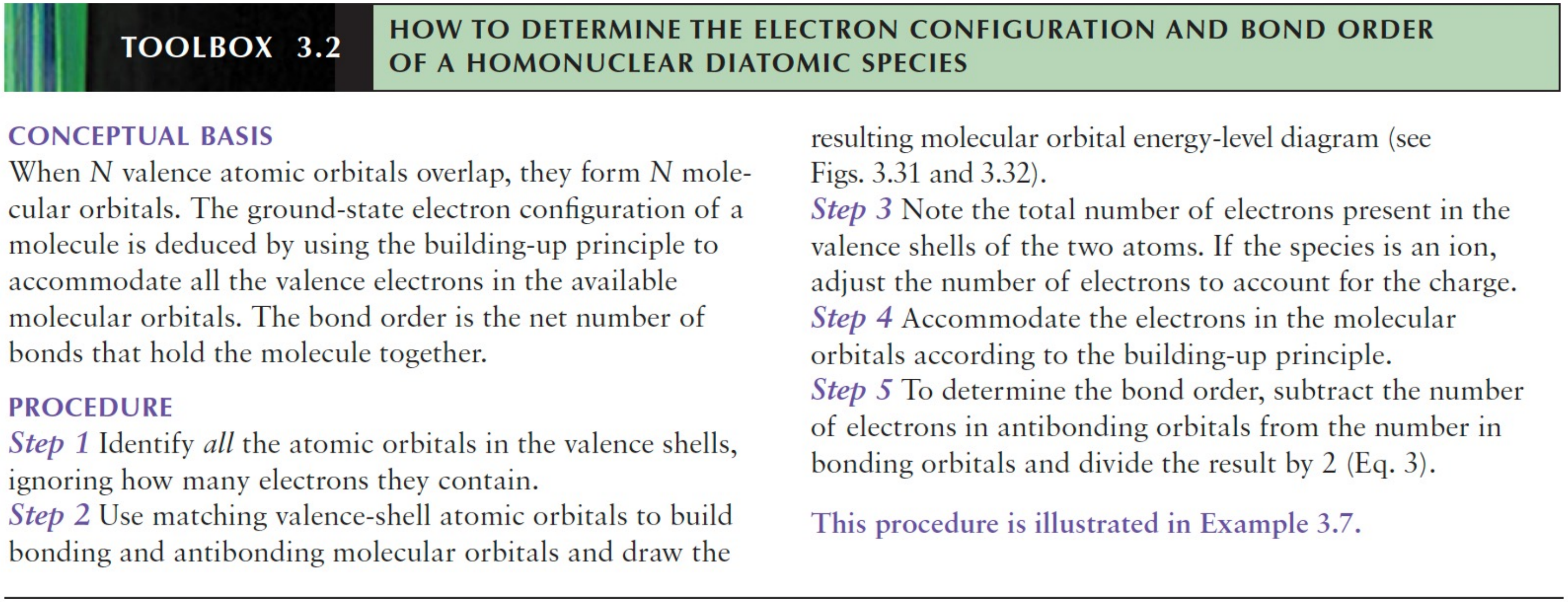
- In N_2, there are eight electrons in bonding orbitals and two in antibonding orbitals:

$$b = \frac{1}{2} \times (8 - 2) = 3$$

This is in agreement with the Lewis structure of N_2.

2G.2 Electron configurations of diatomic molecules

Electron configuration and bond order in MO theory



TOOLBOX 3.2

HOW TO DETERMINE THE ELECTRON CONFIGURATION AND BOND ORDER OF A HOMONUCLEAR DIATOMIC SPECIES

CONCEPTUAL BASIS

When *N* valence atomic orbitals overlap, they form *N* molecular orbitals. The ground-state electron configuration of a molecule is deduced by using the building-up principle to accommodate all the valence electrons in the available molecular orbitals. The bond order is the net number of bonds that hold the molecule together.

PROCEDURE

Step 1 Identify *all* the atomic orbitals in the valence shells, ignoring how many electrons they contain.

Step 2 Use matching valence-shell atomic orbitals to build bonding and antibonding molecular orbitals and draw the resulting molecular orbital energy-level diagram (see Figs. 3.31 and 3.32).

Step 3 Note the total number of electrons present in the valence shells of the two atoms. If the species is an ion, adjust the number of electrons to account for the charge.

Step 4 Accommodate the electrons in the molecular orbitals according to the building-up principle.

Step 5 To determine the bond order, subtract the number of electrons in antibonding orbitals from the number in bonding orbitals and divide the result by 2 (Eq. 3).

This procedure is illustrated in Example 3.7.

2G.2 Electron configurations of diatomic molecules

Summary

The ground-state electron configurations of diatomic molecules are deduced by forming molecular orbitals from all the valence-shell atomic orbitals of the two atoms and adding the valence electrons to the molecular orbitals in order of increasing energy, in accord with the building-up principle.

2G.3 Bonding in heteronuclear diatomic molecules

Heteronuclear diatomic molecules

- For homonuclear diatomic molecules: both atoms contribute equally to a molecular orbital.
- Not the case for heteronuclear diatomic molecules!
- Electronegativities are different: atoms attract electrons in a bond with different strengths.
- Linear combination of heteronuclear diatomic molecules:

$$\Psi = c_A \Psi_\mathrm{A} + c_B \Psi_B$$

- c_A and c_B: weighting coefficients
- Squares of wavefunctions are probability densities: if c_A^2 is large, MO looks more like AO of A; if c_B^2 is large, the MO looks more like the AO of B.
- Atom with AO of lower energy dominates shape of bonding orbital, the electron density is greater on that atom.

2G.3 Bonding in heteronuclear diatomic molecules

Heteronuclear diatomic molecules

- The relative values of c_A^2 and c_B^2 distinguish the type of bond:
- In an **nonpolar covalent** bond, $c_A^2 = c_B^2$, and the electron pair that occupies the orbital is shared equally between the two atoms.
- In an **ionic** bond, the coefficient belonging to one ion, the cation, is nearly zero because the other ion, the anion, captures almost all the electron density of the electron pair that occupies the orbital.
- In a **polar covalent** bond, the atomic orbital belonging to one atom (the more electronegative atom) contributes more to the bonding molecular orbital, and the electron pair that occupies it is more likely to be found closer to that atom than the other atom.

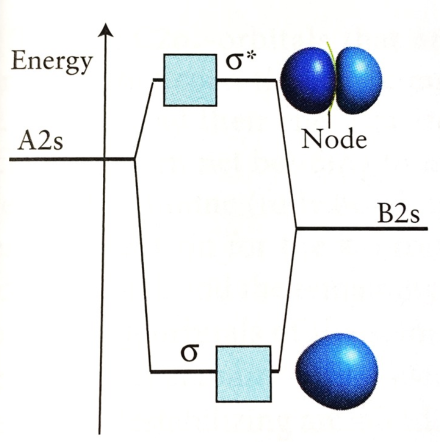


Figure 2G.11 (new book)

2G.3 Bonding in heteronuclear diatomic molecules

Heteronuclear diatomic molecules

- Use same approach as for homonuclear diatomic molecules
- Energy of two atoms will be different
- Mix 2s and $2p_z$ orbitals of both atoms to create σ-orbitals
- Mix $2p_x$ and $2p_y$ orbitals of both atoms to create π-orbitals
- Relative energies are hard to estimate, but can be calculated
- The relative energies of the resulting MOs for NO and CO (X= N or C) are shown in Figure 2G.12

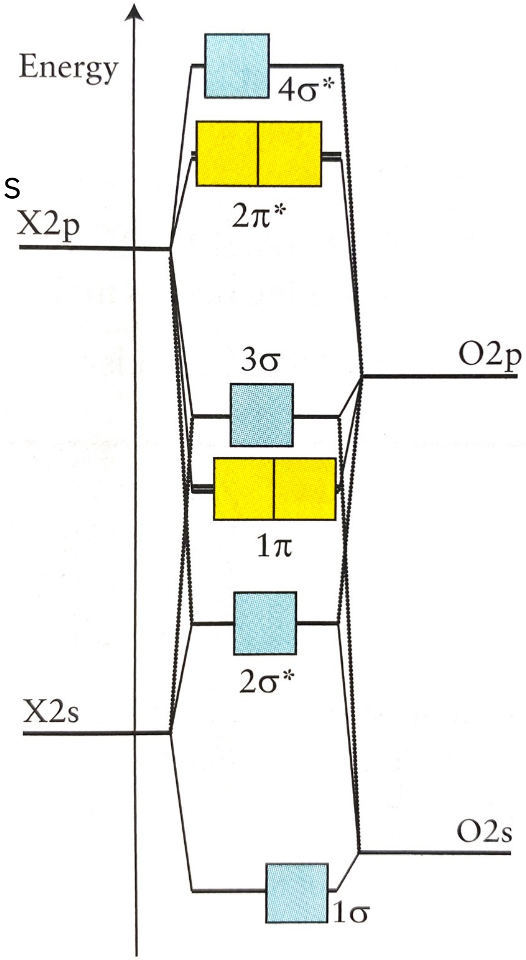


Figure 2G.12 (new book)

2G.3 Bonding in heteronuclear diatomic molecules

Summary

Bonding in heteronuclear diatomic molecules involves an unequal sharing of the bonding electrons. The more electronegative element contributes more strongly to the bonding orbitals, whereas the less electronegative element contributes more strongly to the antibonding orbitals.

2G.5 A comparison of bonding models

Table 2G.1

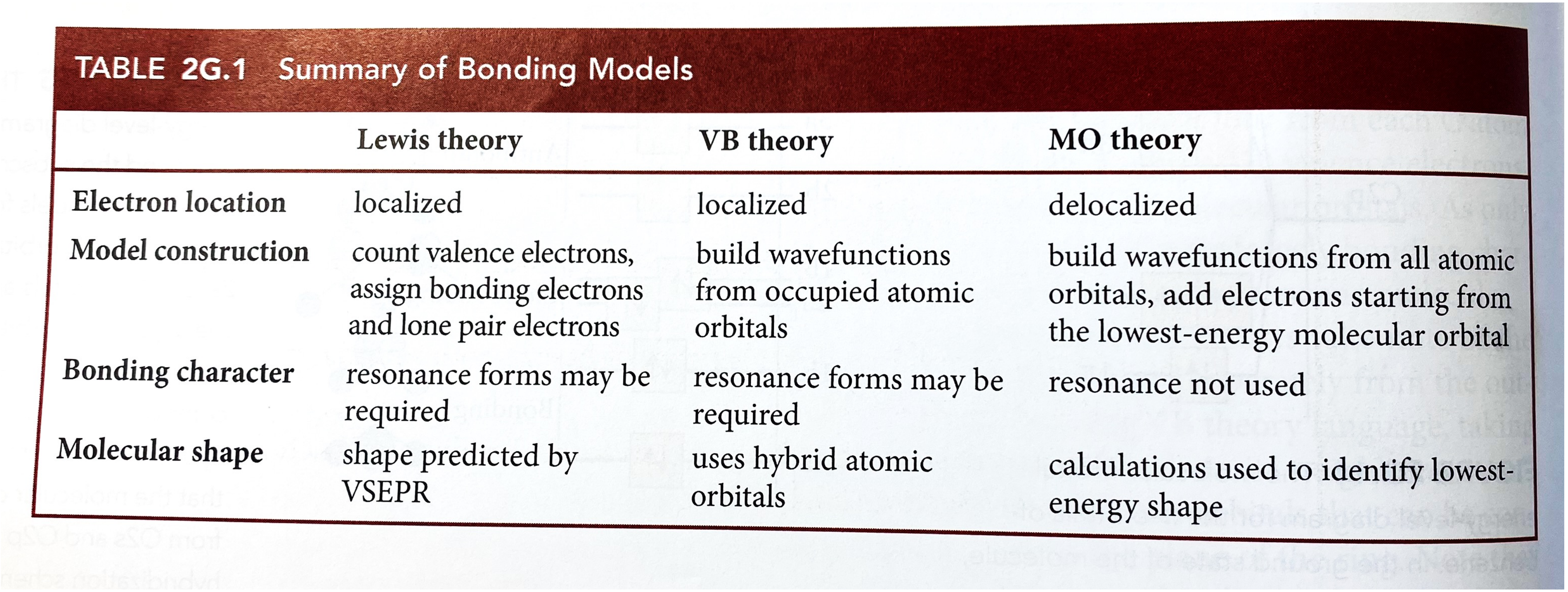


TABLE 2G.1 Summary of Bonding Models

	Lewis theory	VB theory	MO theory
Electron location	localized	localized	delocalized
Model construction	count valence electrons, assign bonding electrons and lone pair electrons	build wavefunctions from occupied atomic orbitals	build wavefunctions from all atomic orbitals, add electrons starting from the lowest-energy molecular orbital
Bonding character	resonance forms may be required	resonance forms may be required	resonance not used
Molecular shape	shape predicted by VSEPR	uses hybrid atomic orbitals	calculations used to identify lowest-energy shape

The skills you have mastered are the ability to

- ☐ Construct and interpret a molecular orbital energy-level diagram for homonuclear diatomic molecules
- ☐ Deduce the ground-state electron configurations of Period 2 diatomic molecules
- ☐ Define and use bond order as an assessment of the number of bonds between pairs of atoms

Summary: You have learned that according to MO theory, bonding is described by wavefunctions (molecular orbitals) that spread over all the atoms in a molecule and that each orbital can be occupied by up to two electrons. You now know about the existence of σ- and π-orbitals and bonding, antibonding, and nonbonding orbitals. Their systematic occupation according to the building-up principle is used to predict the ground-state electron configuration of a molecule. You have seen how MO theory accounts for the paramagnetism of some molecules.